Ordered Phases of Diblock Copolymers in Selective Solvent: Micelle Interactions and Lattice Geometry

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Diblock copolymers in selective solvents are known to aggregate into micelles for copolymer concentration above the critical micelle concentration (CMC). Well above the CMC (volume fractions greater than about 10%) micelles begin to overlap appreciably and interbrush repulsion becomes relevant. To minimize the effect of these interactions, micelles assemble into ordered phases. Recently, thermoreversible transitions between such cubic phases of copolymer micelles have been observed [1]. Here, the thermodynamics of micelle aggregation couples to the strength of the intermicelle repulsions, tuning the relative importance of the constrained micelle entropy and average micelle interactions. We propose a model that captures both these thermodynamics as well as the dependence of micelle repulsion and translational entropy on lattice geometry. This model relies on effective theories for the brush regions of the micelles as well as an Einstein crystal description of the lattice. The core region can be treated as a molten polymer brush while the outer brush must be treated as a semi-dilute polymer brush. This “multi-scale” approach allows us to predict the phase behavior of ordered phases in copolymer solutions under a variety of experimentally realizable conditions. [1] T. P. Lodge, J. Bang, M. J. Park, K. Char, Phys. Rev. Lett. 92, 145501 (2004).